

II.B.6 Control of Catalyst Poisons from Coal Gasifiers

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Objectives

Develop a sorbent system that can reduce the concentration of the three major catalyst poisons (arsenic, iron carbonyl, and nickel carbonyl) present in coal-derived synthesis gas to less than part-per-billion levels.

Introduction

Gasification technologies convert coal and other heavy feedstocks into synthesis gas which can be used in the production of a wide variety of chemicals, high molecular weight liquid hydrocarbons, and waxes. Synthesis gas can also be burned directly as a fuel in advanced power cycles to generate electricity with very high efficiency. However, the coal-derived synthesis gas contains a variety of trace metal contaminants that may poison the catalyst used in the downstream manufacturing processes and may also be regulated in power plant emissions [1]. The heterogeneous catalysts used in the conversion of synthesis gas to hydrogen, methanol and other liquid fuels (e.g., Fischer-Tropsch liquids, dimethyl ether) have been found to be very sensitive even to low levels of arsenic and selenium that are present in the synthesis gas produced by commercial-scale coal gasifiers [2]. Among these contaminants, arsenic poses the largest threat as a catalyst poison due to its high concentration in coal and heavy feedstocks. In addition to being a harmful catalyst poison, arsine could also decompose into arsenic and hydrogen over the surfaces of the cooling train (used to cool the synthesis gas for downstream processing) and

generate an arsenic condensate that not only fouls the heat exchanger tubes but also generates a toxic waste problem. If the synthesis gas is burned to generate power, the control of the emissions of these metals into the environment may also be required.

The project seeks to develop a sorbent system that can reduce the concentration of the three major catalyst poisons (arsenic, iron carbonyl, and nickel carbonyl) present in coal-derived synthesis gas to less than part-per-billion levels. This system will dramatically affect the economics of processes employed to convert coal-derived synthesis gas to liquid fuels by significantly reducing the performance of the catalysts used in these processes.

Approach

The commercially available sorbents developed to date are limited to low temperatures, because they remove contaminants based on physical adsorption [3,4]. Lowering the temperature of the gas to remove contaminants will result in the need to address the following considerations:

1. Expensive heat exchangers and condensers will be required;
2. System efficiency will decrease due to the reduction of mass flow through the gas turbine (depending upon the gasifier type, water vapor may constitute more than half of the synthesis gas stream); and
3. Condensate that is generated may contain many toxic substances need further treatment.

The sorbents developed under this project are designed to operate above the dew point of the synthesis gas, thus eliminating the need for gas cooling as well as the expensive heat exchange equipment. Because the water is maintained in the gas phase, a toxic condensate will not be generated. In addition, the problems associated with arsine decomposition and condensation in the process lines will be eliminated (by carrying out arsenic removal above its condensation temperature).

Accomplishments

- Developed two different sorbents to remove trace metal contaminants including arsenic and selenium from coal-derived synthesis gas.
 - One sorbent can remove arsenic and selenium metals and their hydrides, including arsenic hydride or arsine (AsH_3), selenium hydride (H_2Se) from synthesis gas at elevated temperatures (120-300°C).

- A sulfur tolerant version of the same sorbent that can remove arsenic and selenium from synthesis gas at elevated temperatures (120-300°C) in the presence of up to 10,000 ppmw of hydrogen sulfide (H₂S) and/or carbonyl sulfide (COS).
- Demonstrated in bench-scale experiments that both sorbents could remove arsenic with high capacity and with high efficiency (reducing arsenic concentration to less than 10 ppbv).
- Subcontracted with a leading U.S. catalyst manufacturer to scale-up the production of the new sorbents. The sorbent produced by commercial techniques at large-scale achieved all performance requirements.

Future Directions

The performance of these sorbents will be demonstrated in field tests, employing actual coal-derived synthesis gas.

FY 2006 Publications/Presentations

Paper submitted for presentation at the 23rd Annual International Pittsburgh Coal Conference, September 25-28, 2006, Pittsburgh, PA.

References

1. Quinn, R.; Dahl, T.A.; Toseland, B.A. An Evaluation of Synthesis Gas Contaminants as Methanol Synthesis Catalyst Poisons. *Appl. Catal. A*. 2004, 272, 61-68, and references cited therein.
2. Quinn, R.; Mebrahtu, T.; Dahl, T.A.; Lucrezi, F.A.; Toseland, B.A. The Role of Arsine in the Deactivation of Methanol Synthesis Catalysts. *Appl. Catal. A*. 2004, 264, 103-109.
3. Golden, T.C., Hsuing, T.H., and Synder, K.E., (1991). "Removal of Trace Iron and Nickel Carbonyls by Adsorption", *Ind. Eng. Chem. Res.* Vol. 30, No. 3.
4. Haacke, G.; Brinen, J.S., Burkhard, H. Arsine Adsorption on Activated Carbon. *J. Electrochem. Soc.: Solid State Tech.* 1988, 135, 715-718.